



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Modelling of the mechanical durability of constrained Nafion membrane under humidity cycling

Andreas Theiler, Larisa Karpenko-Jereb*

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Graz, Austria

ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form

30 March 2015

Accepted 16 May 2015

Available online 13 June 2015

Keywords:

Modelling

Nafion membrane

Humidity cycling

Mechanical durability

Deformation energy

ABSTRACT

Several degradation processes limit the lifetime of polymer electrolyte membranes in fuel cells. One of these processes is humidity changes during the operation of the cell, which causes swelling and shrinking of the polymer electrolyte membrane. Changes in membrane size lead to periodic mechanical stresses, which damage the polymer. This damage leads to the formation of cracks in the membrane and, thus, results in early failure of the fuel cell.

This study presents a theoretical model that predicts the membrane lifetime depending on the thickness of the membrane and operating conditions of the periodic humidity cycle such as: amplitude of the humidity variation in the cycle, cycle duration, and temperature. The model is based on the assumption that mechanical destruction of the polymer electrolyte membrane, constrained in the fuel cell, occurs when the deformation energy applied to the membrane reaches a maximum value. The mechanical stress and deformation energy are estimated using the modified Eyring equation [Burlatsky et al., 2012]. The proposed model takes into account the influence of the temperature and water concentration on the membrane mechanical properties. The water concentration in the membrane is simulated by considering the water sorption/desorption kinetics and water sorption isotherm of the membrane.

The model was used to predict the lifetime of the non-reinforced membrane Nafion. The calculation results show that membrane mechanical durability correlates positively with increasing membrane thickness and temperature. The increase in the amplitude of the humidity cycle decreases membrane mechanical durability. At very short humidity cycles (≤ 50 – 100 s), the membrane lifetime declines with increasing period of the humidity cycle. At higher humidity cycle period (> 50 – 100 s), the increase of the cycle duration leads to continuous growth of the membrane lifetime.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +43 316 873 32241; fax: +43 316 873 32202.

E-mail addresses: andreas.theiler@student.tugraz.at (A. Theiler), larisa.karpenko-jereb@tugraz.at (L. Karpenko-Jereb).
<http://dx.doi.org/10.1016/j.ijhydene.2015.05.110>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Nomenclature			
<i>Latin symbols</i>		$\bar{\lambda}$	average water concentration in the membrane
A	area, m^2	λ_{mem}	water concentration inside membrane
C_1	integration constant	λ_{sur}	water concentration on the membrane surface
C_2	integration constant, 1/s	λ_0	starting water concentration in the PEM
E	Young's modulus, Pa	σ	tension, Pa
F	force, N	σ_x	tension parallel to the membrane surface, Pa
f	frequency, Hz	τ_{period}	cycle period, s
k_B	Boltzmann's constant, J/K	ϕ_{relax}	polymer relaxation time, s
L	membrane thickness, μm	<i>Superscripts and Subscripts</i>	
N	mechanical membrane lifetime, cycles	abs	absorption
N_h	mechanical membrane lifetime, h	def	deformation
q_T	amount of heat energy in a polymer entanglement, J/m^3	des	desorption
RH	relative humidity, %	exp	value from experimental data
s	distance in direction of F, m	max	related to a maximal value
T	temperature, $^{\circ}C$	mem	membrane
t	time, s	min	related to a minimal value
V	volume, m^3	sim	value obtained by simulation
V_{rel}	relative volume of an entanglement, m^3	sur	surface of the membrane
w	specific energy, J/m^3	x	direction parallel to the surface of the PEM
$\bar{w}_{def,max}$	mean maximal deformation energy, J/m^3	<i>Abbreviations</i>	
<i>Greek symbols</i>		CFD	computational fluid dynamics
α	dimensional change coefficient	MEA	membrane electrode assembly
ϵ	elongation	NMR	nuclear magnetic resonance
ϵ_x	elongation of the PEM in direction x	PEM	polymer electrolyte membrane
		PEMFC	polymer electrolyte membrane fuel cell

Introduction

The mechanical stability of proton exchange membranes is one of key factors limiting the life expectancy of low temperature fuel cells [1–3]. During the last two decades, numerous experimental and theoretical studies have been performed in order to investigate the mechanical properties of proton exchange membranes in PEMFC and to identify influential factors [1,4–34].

The experimental investigations [11–15] showed that the Young's modulus of Nafion membranes decreases as the membrane hydration level and temperature increase. The papers [20,23] report the results of studies on the influence of the strain rate of Nafion, performed at various humidity levels and temperatures. The true stress in the membrane declines as a degree of polyelectrolyte swelling and temperature increases. Similar results have been observed for the yield stress.

The works [31–34] discuss the experimental results on Nafion membrane relaxations obtained using the dielectric spectroscopy and dynamic mechanical analysis at various temperature and relative humidity. The following relaxations were detected in the sulfo-cationic perfluorinated polymer electrolytes: α -relaxation (at $f \sim 10^0$ – 10^1 Hz) is related to the mobility of the ionomer main and side chains via thermally activated destabilization of the electrostatic interactions; β -relaxation (at $f \sim 10^4$ – 10^5 Hz) is associated with the motion of

side chains; while γ -relaxation is attributed to local motions of the fluorocarbon –CF₂- backbone segments. Nafion shows stiffening for temperatures and relative humidities above 90 $^{\circ}C$ and 60%, which is related to α -relaxation [32].

In order to describe the stress behavior of Nafion under different conditions, such as various levels of strain or types of hydro thermal cycling, several models have been presented in the past [1,18–26].

Solasi et al. [16] proposed a nonlinear, time-dependent, constitutive model to predict the hydro-thermo mechanical behavior of Nafion membrane. The two-layer viscoplasticity model, which consisted of elastoplastic and elastic-viscous networks, takes into account the rate-dependent and rate-independent behavior of the polyelectrolyte. The model calculations of the mechanical stress in the membrane at different strain rates were found to agree satisfactorily with the relation test results.

Bogachev et al. [9] developed a linear elastic–plastic 2D finite elements model and applied this model to analyze the mechanical stress distribution in MEA taking into account the clamping condition in the fuel cell. The study showed that a maximum and strongly heterogeneous mechanical stress was observed under the junction seal joint/graphite plate in the membrane.

Al-Baghdadi [18] studied the hydro-thermal stress distribution in PEM fuel cells under regular operating conditions by using a CFD simulation. The obtained results demonstrated

that the non-uniform distribution of the stresses is due to the temperature gradient in the cell. This contributes to delamination between the membrane and the gas diffusion layers, especially at the cathode and can lead to the formation of cracks during steady-state performance of the fuel cell.

Silberstein et al. [23] characterized the elastic–plastic behavior of Nafion membrane with monotonic and cycling uniaxial tension testing as a function of strain rate, temperature, and hydration. Based on the experimental data obtained, they developed a constitutive model that describe the mechanical behavior of the Nafion membrane under monotonic and cyclic loading profiles in the fuel cell. The simulation at 25°C showed that the stress-strain behavior remains elastic–plastic for all hydrated states and that the yield stress decreases with increasing hydration and temperature.

In their paper [25], Silberstein et al. proposed a three-dimensional constitutive model. The model was applied to describe mechanical stress by taking into account the biaxial loading profile under hydro-thermal cycling conditions, which occur when the membrane is highly constrained in an in-plane direction and relatively unconstrained in the through-thickness direction.

Klein et al. [28] investigated a correlation between the elasticity of Nafion and its water self-diffusion coefficient. Using pulsed-field gradient NMR, the single membrane was measured under traction. The study demonstrated that a membrane held under high tension displayed much higher water diffusion anisotropy than the non-stretched one. In order to interpret the experimental data, Klein et al. adapted a pseudo affine deformation model on Nafion membrane and simulated the orders of change in parameters of the membrane held under traction. Results showed that the estimated micro structure parameters were in agreement with data reported in the literature from small angle scattering experiments.

Burlatsky et al. [1] combined an extended Eyring model of polymer deformation with a damage accrual model based on maximum stress in order to estimate the lifetime of a perfluorinated membrane GoreSelect® under conditions of humidity cycling in the fuel cell. The calculation showed that at 78°C and a constant humidity on the cathode and humidity cycling conditions on the anode, the membrane lifetime increased as the minimal relative humidity level of the cycle increased.

The present work describes a mathematical model that was developed to predict the mechanical durability of Nafion type membranes while taking into account the influences of the membrane thickness and humidity cycling conditions such as cycle duration, humidity amplitude, and temperature.

Materials

This work addresses non-reinforced Nafion membranes and their properties, which were observed and for which data has been published in the literature. The developed model considers only mechanical effects on the life expectancy of the membrane and disregards the effects of chemical degradation.

Theory

Assumptions

The developed model that predicts the mechanical durability of Nafion membrane is based on the following assumptions:

1. Mechanical destruction of the PEM, which is constrained in the fuel cell, occurs when the deformation energy, caused by mechanical stress in the membrane, achieves a maximal value.
2. The mechanical stress in the membrane is considered only in one direction, parallel to the membrane surface.
3. The maximal value of the deformation energy is determined by considering mechanical characteristics of the polymer such as Young's modulus, and elongation and polymer constants.
4. Membrane elongation is a function of membrane water concentration λ_{mem} .
5. The model takes into account the fact that the Young's modulus of the polymer membrane increases as the equilibrium level of the relative humidity and temperature decreases and does not change over time.
6. The water concentration in the membrane is simulated by taking into account the kinetics of the water sorption/desorption processes in the membrane and the water sorption isotherm – the dependence of the membrane water concentration on the relative humidity level.
7. The influence of temperature on the water sorption/desorption processes were neglected.
8. The auxiliary equations describing the mechanical properties [Young's modulus, water sorption/desorption kinetics, elongation) were modelled on the basis of experimental data published for non-reinforced perfluorinated membranes Nafion [8,13].
9. The presented model was developed for the temperature range $20^{\circ}\text{C} \leq T \leq 90^{\circ}\text{C}$.

Physical model

The variation in humidity leads to a change in the water concentration λ_{mem} of the polymer electrolyte membrane, causing swelling or shrinking of the membrane film. Fig. 1 demonstrates alterations in the elongation and tension of non-constrained and constrained membranes at different membrane water concentrations. When the level of humidity

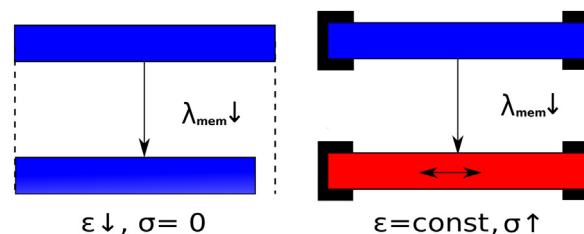


Fig. 1 – Swelling and tension in a non-constrained membrane (left) and a constrained membrane (right).

decreases the water concentration and length of the unconstrained membrane decreases (Fig. 1, on the left). In a real fuel cell, however the membrane is constrained and cannot change its length. Therefore, when the humidity decreases the constrained membrane enters a stretched state. In this case, the alteration of the membrane water content leads to the development of mechanical stress inside the membrane (Fig. 1, on the right). During humidity cycling in the fuel cell, the mechanical stress on the membrane constantly varies, deforming and gradually damaging the polymer film. After a certain amount of time, this results in membrane failure (Fig. 2). The energy provided by the stress, resulting in a deformation of the membrane, is called deformation energy. The amount of membrane damage caused by mechanical stress can be characterized by this deformation energy. The complete damage of the polymer membrane occurs when the deformation energy reaches a certain maximal value, as shown in Fig. 2. This maximal value of the deformation energy depends on the mechanical properties of the polymer such as described by Young's modulus, and the elongation and polymer constants.

Governing equations

Deformation energy. In accordance with the laws of mechanics, when the membrane is exposed to stress, this stress will deform the membrane. The level of this deformation can be measured by the deformation energy supplied to the membrane (in other words: the membrane absorbs the deformation energy during the mechanical stress).

The deformation energy w_{def} absorbed over the time t is calculated by [35]:

$$w_{def} = \int_0^t \sigma_x \frac{d\varepsilon_x}{dt} dt \quad (1)$$

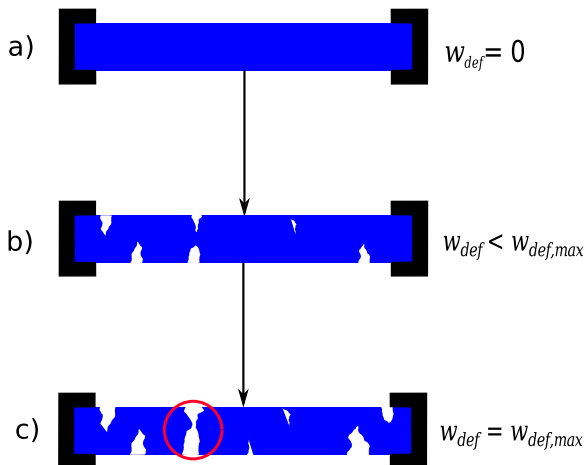


Fig. 2 – Damage of the membrane after a) no deformation b) absorbing a amount of deformation energy smaller than the maximum deformation energy c) absorbing the maximum amount of deformation energy. The polymer is too damaged for further use.

Where σ_x is the tension in the membrane parallel to the surface and ε_x is the membrane elongation in the direction of x .

Tension. The tension arising in the membrane during humidity cycling is calculated by using (2), proposed by Burlatsky et al. [1].

$$\frac{d\sigma_x(t)}{dt} = E \left. \frac{\partial \varepsilon_x(t)}{\partial t} \right|_{\lambda} + E\alpha \frac{d\Delta\lambda(t)}{dt} - \frac{q_T}{\phi_{relax}} \sinh\left(\frac{\sigma_x(t)}{q_T}\right) \quad (2)$$

They derived equation (2) from the extended Eyring model for viscous materials.

The first term on the right side of the equation is zero in a constrained membrane. In this equation, σ_x is the tension in the x -direction, E is Young's modulus, which is described below, α is the dimensional change coefficient, q_T is an empirical material constant, also described below, and ϕ_{relax} is the polymer relaxation time. The proposed model considers the general stress relaxation time according to the Maxwell model for viscoelastic materials [35]. According to the findings published in [31–34], the relaxation considered in the present model can be attributed to α -relaxation, which is caused by the mobility of the Nafion main and side chains.

ϕ_{relax} was calculated from the data appearing in Lu et al. [26] and is shown in Table 1. $\Delta\lambda$ is the difference between the mean water concentration $\bar{\lambda}$ and the current water concentration $\lambda_{mem}(t)$ in the membrane at time t :

$$\Delta\lambda(t) = \lambda_{mem}(t) - \bar{\lambda} \quad (3)$$

By integrating (2) over the time, the following integral equation for σ_x is obtained, assuming that the elongation and tension is zero at time zero:

$$\sigma_x(t) = E \alpha \Delta\lambda - \frac{q_T}{\phi_{relax}} \int_0^t \sinh\left(\frac{\sigma_x(t)}{q_T}\right) dt \quad (4)$$

The extended Eyring model considers Nafion to be a series of polymer chains which are knotted together in entanglements [1]. Some polymer chain links are able to slip out of the entanglement. The probability of this event can be characterized by q_T and is defined as the heat energy $k_B T$ per volume of the entanglement V_{rel} .

$$q_T = \frac{k_B T}{V_{rel}} \quad (5)$$

Burlatsky et al. [1] determined V_{rel} for a perfluorinated membrane GoreSelect[®] (Table 1). This value was taken for the simulation with Nafion membrane.

Table 1 – Model constants which are used in the present model.

Symbol	Value	Ref.
ϕ_{relax}	125 s	[26]
V_{rel}	$2.85 \cdot 10^{-27} \text{m}^3$	[1]
α	0.124	[8]
k_B	$1.38 \cdot 10^{-23} \text{JK}^{-1}$	

Auxiliary equations

Humidity cycling. The model considers changes in humidification that are equal on both sides of the membrane. In this work, the alteration in humidity was modelled by using a rectangular function. For the simulation, experimental data [11,36] were selected. In these papers, the PEM lifetime was studied when subjected to humidity cycling under conditions of “hopping” humidity changes, ranging between a maximum to a minimum humidity level. These experimental conditions correspond to the rectangular function of the variation in humidity.

Membrane water concentration. The mathematical model approach is based on the assumption that the water concentration in the membrane is constant throughout the membrane. This assumption was made on the basis of experimental observations [13], which revealed that the water diffusion through the bulk of the membrane occurs significantly more quickly than the water diffusion through the membrane surface/gas boundaries. The time-dependent changes in the membrane water concentration are proportional to the differences between the water concentration λ_{sur} directly on the membrane surface and inside the membrane λ_{mem} :

$$\frac{d\lambda_{mem}}{dt} \propto \lambda_{sur} - \lambda_{mem} \quad (6)$$

The solution for this differential equation is

$$\lambda_{mem} = \lambda_{sur} + C_1 e^{C_2 t} \quad (7)$$

To determine the constant C_1 the following conditions were used.

$$\begin{aligned} \lambda_{mem}(t=0) &= \lambda_0 \\ \lambda_{mem}(t=\infty) &= \lambda_{sur} \quad \text{with } \lambda_{sur} = \text{const.} \end{aligned} \quad (8)$$

where λ_0 is the water concentration in the membrane at $t=0$. This leads to

$$\lambda_{mem} = \lambda_{sur} + (\lambda_0 - \lambda_{sur})e^{C_2 t} \quad \text{with } C_2 < 0 \quad (9)$$

The water concentration on the membrane surfaces is a function of the relative humidity, RH. For the calculation of λ_{sur} , a linear approximation [1] for the water sorption isotherm was applied:

$$\lambda_{sur} = RH \cdot 9 + 3 \quad (10)$$

Inserting (10) in (9) yields

$$\lambda_{mem} = 9RH + 3 + (\lambda_0 - 9RH - 3)e^{C_2 t} \quad \text{with } C_2 < 0 \quad (11)$$

In order to find out the integral coefficient C_2 , and identify the dependence of the coefficient on the membrane thickness, the experimental data of Satterfield and Benziger [13] were analyzed. At present, the paper is a unique study devoted to a systematic analysis of the influence of the membrane thickness and temperature on the water absorption/desorption kinetics of the perfluorinated polymer electrolytes. The measurements were performed on the Nafion membranes with quite large thicknesses (51, 127, 254, 606, μm), that are atypical for the application in realistic fuel cells. Perhaps the decision for thick membranes was the fact that

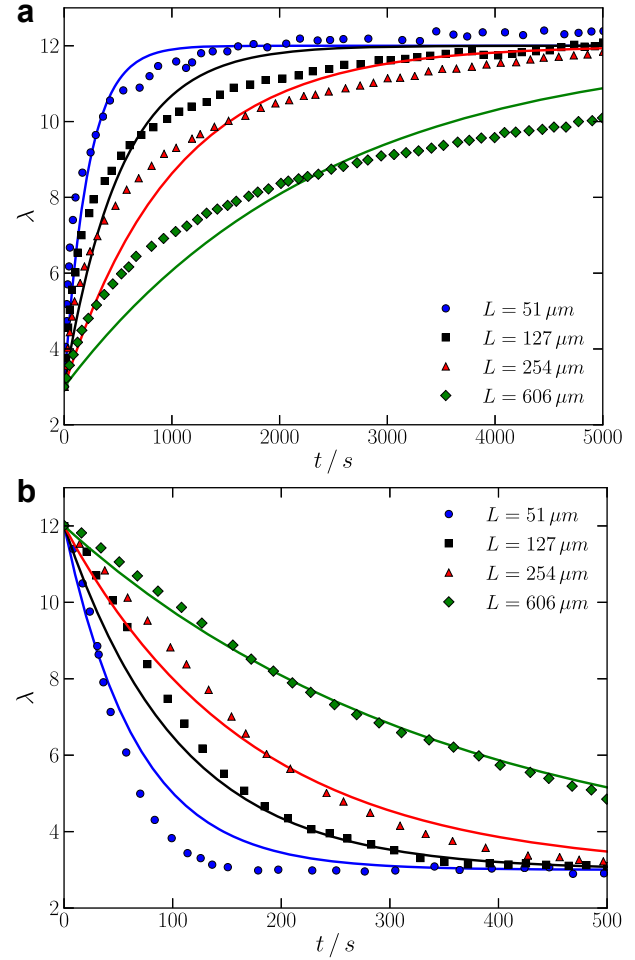


Fig. 3 – Data from Satterfield and Benziger [13] and fitting functions (black lines) for the water a) absorption and b) desorption kinetics of Nafion.

such kind of the tests are very challenging for thin polymer films, and the accuracy of the measurements dramatically decreases with lowering membrane thickness and sample weight. They noted that the water diffusion of water vapor across the membrane interface is significantly slower than that inside of the membrane and, therefore, is a limiting factor for the water ab- and desorption rates. The experimental data on water absorption for Nafion membranes are presented in Fig. 3 a). The dependences of the water absorption vs. time were described by the exponential equation (11), where the value C_2^{abs} was fitted to each membrane thickness, thus, that the fitting curve has a satisfactory correlation with the corresponding experiment. The exponential function (11) allows describing the experiments using only one variable C_2 , which takes into account the influence of the polymer electrolyte thickness on the sorption processes. The same procedure was carried out for water desorption kinetics to determine the values of coefficient C_2^{des} (Fig. 3 b)).

The negative inverse values of coefficients C_2 as a function of membrane thickness are described adequately by the linear equations (Fig. 4):

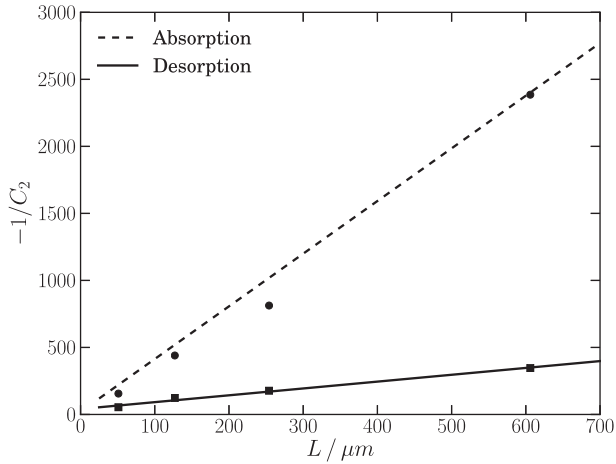


Fig. 4 – Fit of the coefficients $-1/C_2$ over the thickness of the membrane for absorption (dashed line), and desorption (solid line). The dots are the fitted values of $-1/C_2$ from eq. (11) (Fig. 3a) and b)).

$$-\frac{1}{C_2^{abs}} = 3.92 \cdot L + 20.8 \quad \text{for absorption} \quad (12)$$

$$-\frac{1}{C_2^{des}} = 0.510 \cdot L + 40.8 \quad \text{for desorption} \quad (13)$$

The fits (12) of the absorption parameters are quite accurate for membrane thicknesses of ca. $50 \mu\text{m}$. For water desorption kinetics, equation (13) matches more exactly for thicknesses of ca. $600 \mu\text{m}$. Despite the fact that the fits are not completely accurate for some thicknesses, the fit coefficients were used, in order to keep the model simple. However we are planning to improve this part of our model by using a more detailed water transport model [37] in the future.

Elongation of the PEM membrane. To calculate the dimensional change of the membrane due to swelling caused by variations in water concentration, a linear correlation between elongation and water concentration was drawn:

$$\varepsilon_x(t) = \alpha \cdot \lambda_{mem}(t) \quad (14)$$

Where ε_x is the elongation of the membrane, which is defined as change in length over original length and α is the dimensional change coefficient. According to the measurements of Tang et al. [8], the dimensional change coefficient is listed in Table 1.

Young's modulus. Young's modulus, E , is a measure of the tensile characteristics of an elastic material.

For Nafion, the value of Young's modulus essentially depends on the temperature and water concentration of the material. Tang et al. investigated the Young's modulus of Nafion at different temperatures and levels of relative humidity [8] (Fig. 5). They analyzed E at four different temperatures ranging from 25°C to 85°C and at four levels of relative humidity, ranging from 30% to 90%.

For our calculations, the data of Tang et al. were fitted using a linear function for each RH. For the calculation of Young's modulus at arbitrary levels of relative humidity, the fitted parameters were linearly interpolated or extrapolated:

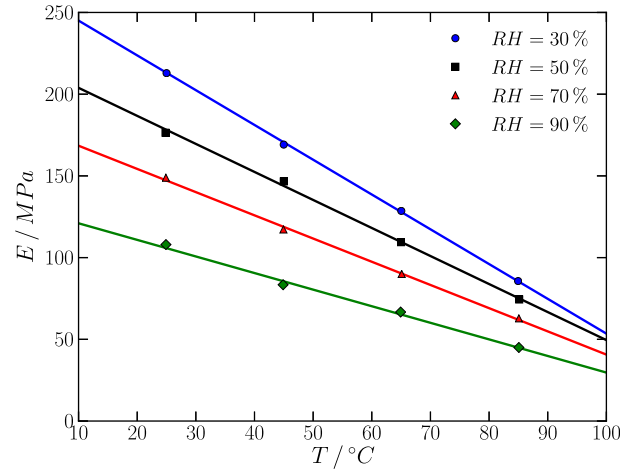


Fig. 5 – Young's modulus as a function of temperature for different relative humidity levels. The points represent experimental data reported by Tang et al. [8]. The lines are the fitted linear functions.

$$E = ((0.0281 \cdot RH - 2.66)T + (-2.22 \cdot RH + 333)) \cdot 10^6 \quad (15)$$

Simulation results and discussion

The developed model of the lifetime of Nafion membranes was programmed using a Python code. The program contains the three main sub-routines:

1. The calculation of the membrane water concentration
2. The estimation of the tension caused by humidity cycling
3. The calculation of the deformation energy absorbed by the membrane and mechanical durability

Humidity cycling was realized using a rectangular function as described in the previous section, with a constant period τ_{period} and at a constant relative humidity change amplitude of $(RH_{min} + RH_{max})/2$.

Maximal deformation energy. In this model, it is essential to estimate the maximum deformation energy that non-reinforced Nafion can absorb before the membrane fails to function properly. For this reason we scrutinized several experiments that had been conducted to estimate the lifetime of Nafion membranes under conditions of humidity cycling.

These experimental data are summarized in Table 2. For these known experiments the maximal deformation energy was calculated using equation (1). The diversities of results obtained may be due to the different criteria that were used to determine the failure of the PEM in the experiments and due to the different experimental techniques. The average value of the maximal deformation energy is:

$$\bar{w}_{def,max} = 25 \cdot 10^6 \frac{\text{J}}{\text{m}^3} \quad (16)$$

Mechanical durability. The model was applied to investigate the influence of thickness and operating conditions of periodic humidity cycling such as:

Table 2 – Literature data from humidification cycling experiments and calculated maximal deformation energy.

Ref.	$RH_{min}/RH_{max}/\%$	τ_{period}/s	$T/^\circ C$	$L/\mu m$	Material	$N/cycles$	$w_{def,max}/J/m^3$
[7]	30/80	1800	65	25	Nafion NR111	100	$22.1 \cdot 10^6$
[11]	0/100	600	90	25	Nafion N111	100	$36.5 \cdot 10^6$
[36]	0/100	7200	100	50	Nafion N112	50	$15.4 \cdot 10^6$

- Temperature
- Amplitude of the humidity variation in the cycle
- Cycle duration

Figs. 6–7 illustrate the simulation results for the membrane lifetime duration with various membrane thicknesses and under different humidity cycling operating conditions. Fig. 6 displays the lifetime of Nafion membranes with various thicknesses as a function of the minimal RH_{min} of the humidification cycle ($\tau_{period}=5\text{ min}$), whereby the maximal relative humidity was kept constant at 100%. The model results show a pronounced increase in the membrane lifetime at the minimal relative humidity of the cycle, from around 60 to 99%. It should be mentioned that the change of RH_{min} from 60 to 90% leads to an increase in the membrane lifetime of one order of the magnitude, and an even greater increase is observed when RH_{min} is changed from 90 to 99%. The increasing temperature correlates positively with an increase in the mechanical durability of the membrane (Fig. 7). For the humidification cycle $RH_{min}/RH_{max}=70/100\%$, $\tau_{period}=5\text{ min}$, a slight increase in the expected membrane lifetime was observed for membranes with thicknesses of 10, 25, and $35\ \mu m$, while the membrane with a thickness $50\ \mu m$ showed a stronger temperature dependence. The overall low dependence of the lifetime on temperature is caused by the fact, that the model considers only the temperature dependency of Young's modulus and neglects the temperature dependency of the water absorption kinetics.

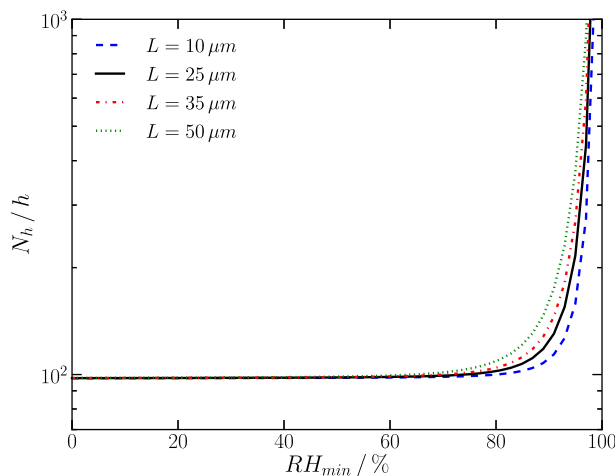


Fig. 6 – The predicted mechanical lifetime of Nafion membranes of different thicknesses as a function of the minimal relative humidity in the cycle. The simulations were performed for the conditions: $T=70^\circ C$, $RH_{max}=100\%$ and $\tau_{period}=5\text{ min}$.

Fig. 8 presents the simulation results of the expected lifetime of Nafion membranes with a thickness of $25\ \mu m$ as a function of the humidity cycle duration measured in hours a,b) and in cycle number c,d). As seen from the plots, the dependence of the expected membrane lifetime on the period of the humidification cycle passes through a minimum at τ_{crit} , which is found between ca. 50 to 150s, depending on the average humidity level $(RH_{min}+RH_{max})/2$ value and the amplitude $(RH_{max}-RH_{min})$ of the cycle.

Fig. 8 a,c) display the mechanical durability of the membrane at the same amplitude of the variation humidity ($RH_{max}-RH_{min}=20\%$) in the cycle. As seen from the figure a), the expected lifetime of Nafion membrane increases with growing average humidity level. Fig. 8 b,d) illustrate the mechanical durability of the membrane at different amplitudes of the humidity cycle. The results show that an increase of the humidity cycle amplitudes leads to a decrease in the membrane mechanical lifetime, whereby a more pronounced effect is observed for short cycle periods ($\leq 50-100\text{ s}$).

Fig. 8 a,b) show, that the Nafion mechanical lifetime expressed in hours goes through minima. For $5\text{ s} \leq \tau_{period} \leq \tau_{crit}$ the membrane lifetime decreases with increasing cycle duration. During such short cycle intervals the membrane is not able to absorb or desorb water to its equilibrium value, which is predicted by the water sorption isotherm (10). With increasing cycling duration, the water concentration variations are growing and the mechanical damage related to the membrane swelling/shrinking increases. At the minimum of the membrane mechanical lifetime, observed in Fig. 8 a,b), the

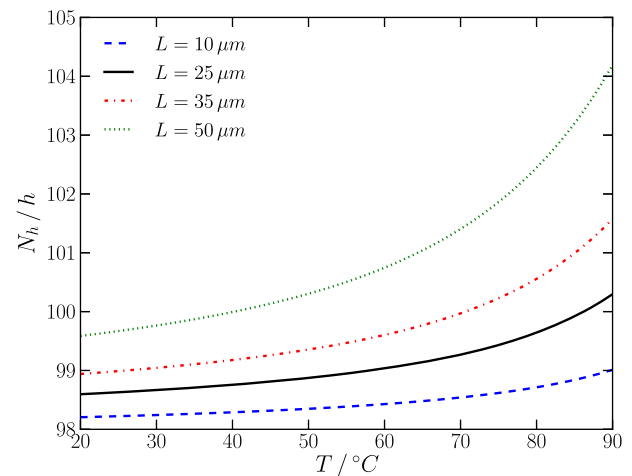


Fig. 7 – The predicted mechanical lifetime of Nafion membranes with various thicknesses as a function of temperature. The simulations were performed for humidity cycle $RH_{min}/RH_{max}=70/100\%$ with period $\tau_{period}=5\text{ min}$.

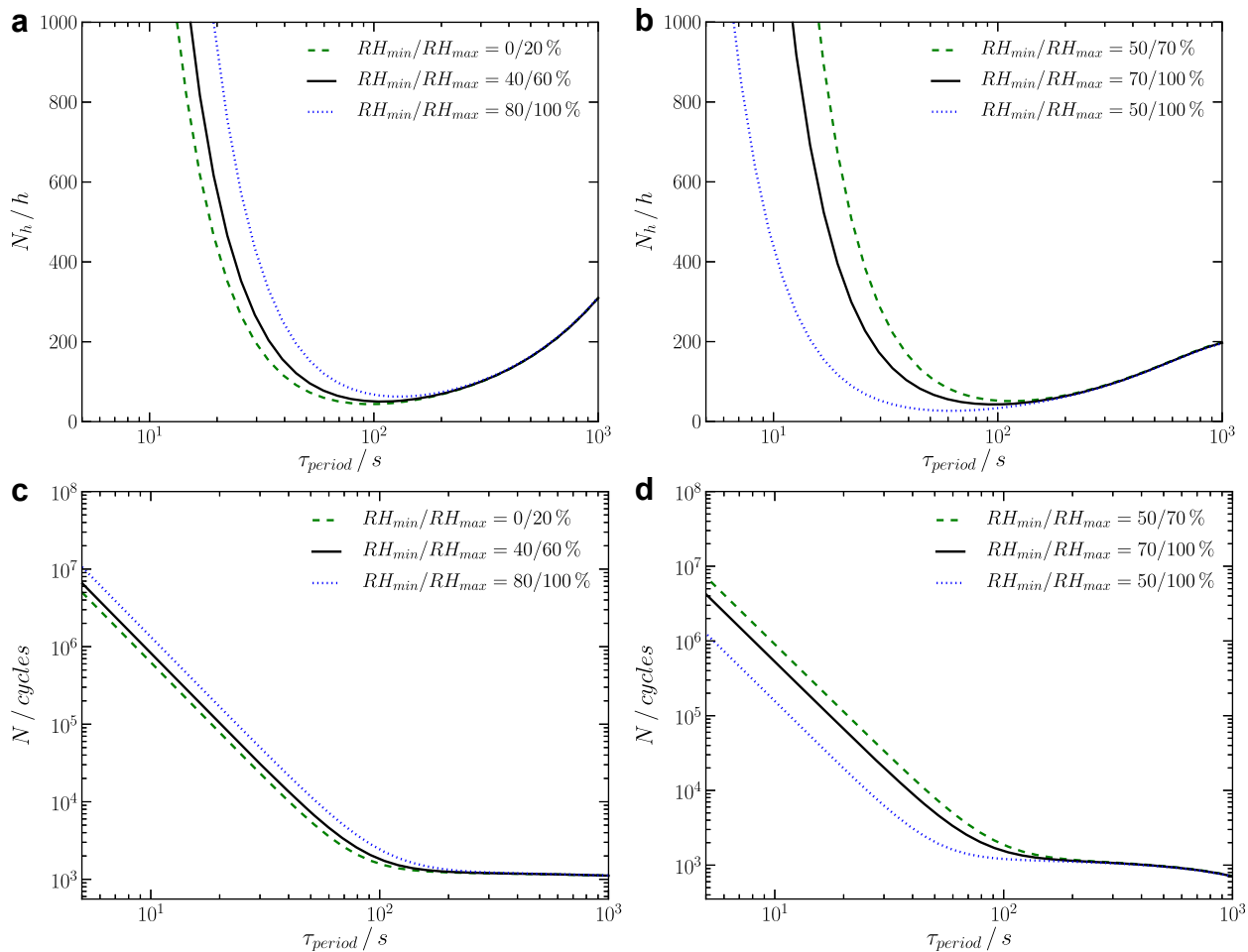


Fig. 8 – The predicted mechanical lifetime of Nafion membrane ($L=25\ \mu\text{m}$) as a function of the humidity cycle period: The plots a, b) show the lifetime in hours and c, d) show the lifetime as number of full humidity cycles. The simulations were performed at a temperature of $T=70^\circ\text{C}$ and various amplitudes of the relative humidity cycle a, c) $RH_{\min}/RH_{\max}=0/20; 40/60; 80/100\%$ and b, d) $RH_{\min}/RH_{\max}=50/70; 70/100; 50/100\%$.

water concentration changes are reaching their maximum values, defined by the sorption isotherm as well by RH_{\min} and RH_{\max} . At the minimum of the mechanical lifetime, observed in 8 a,b), the damage dealt per time reaches its maximum. At $\tau_{\text{period}} > \tau_{\text{crit}}$ the damage caused per cycle stays practically constant, this leads to an approximately linear increase of the lifetime.

Fig. 8 c,d) demonstrate, that the predicted mechanical lifetime, measured in number of RH cycles, stays almost at the same level for $\tau_{\text{period}} > \tau_{\text{crit}}$ and decreases only slightly. This slight change can be explained by mechanical relaxation. Although the swelling changes are at their maximum value, the mechanical relaxation process is not fully completed after τ_{crit} . Thus, the damage due to mechanical relaxation per cycle still increases with the cycle duration. This relaxation causes additional damage to the membrane, but it is noticeable smaller than the damage caused by the membrane swelling/shrinking.

Currently, systematic investigations on the Nafion mechanical lifetime as a function of RH cycle condition, temperature and membrane thickness, which could be used for an adequate validation of the presented model, are missing.

Nevertheless we found a few experimental measurements [38–40], which we used to carry out a preliminary justification of the model. Table 3 displays the experimental values [38–40] of the membrane lifetime and operating conditions in these tests. Panha et al. [38] and Aindow et al. [40] investigated the mechanical durability of the commercial perfluorinated Gore membranes of $30\ \mu\text{m}$ thickness under relative humidity cycling in single fuel cells. Macauley et al. [39] performed an accelerated durability test for Nafion NR211 ($25\ \mu\text{m}$) in a stack design. The tests are arranged in Table 3 according to increasing amplitude of the RH cycle, cycle duration and membrane thickness. The last column of the table demonstrates the magnitudes of the membrane durability calculated using the present model. Although the model considers a single constrained membrane (without catalyst layers) and assumes homogeneous distribution of the water content in the membrane interface, that does not completely correspond to the effects in realistic fuel cells, the simulated results agree qualitatively with the experiments. The calculated values in Table 3 and the data of Figs. 6 and 8 b) show that the membrane lifetime increases with decreasing amplitude of the

Table 3 – Comparison of predicted lifetime N_h^{sim} of unreinforced Nafion with the experiments N_h^{exp} reported in [38–40].

Ref.	$RH_{min}/RH_{max}/\%$	τ_{period}/s	$T/^\circ C$	$L/\mu m$	Material	N_h^{exp}/h	N_h^{sim}/h
[38]	0/100	150	70	25	Gore 57, MEA	450	50
[39]	80/100	600	85	30	NR211, MEA	298	202
[40]	30/90	3120	60	30	Gore PRIMEA, MEA	3500	772

relative humidity, what is well confirmed by the experimental results. The experiments also approve model predictions that the membrane durability grows with increasing RH cycle duration and membrane thickness as demonstrated in Figs. 6–7, 8 b), Table 3. The pronounced deviation of the simulated results for Gore membranes from the experimental values are most likely related to the reinforcement of the Gore membranes. As well known the reinforcement significantly improves the membranes mechanical stability. The investigation reported in [41] showed that the reinforced perfluorinated membrane works in the fuel cell around six-times longer until it fails compared to non-reinforced membranes. As shown in Table 3, the present calculations deviate by the factors 9 and 5 from the experiments reported by Panha [38] and Aindow [40] correspondingly.

Conclusion

This study describes the development of a theoretical model predicting the mechanical durability of the perfluorinated membrane Nafion used in a polymer electrolyte fuel cell under conditions of periodic humidity cycling. The model is based on the assumption that mechanical damage to the polymer electrolyte membrane constrained in the fuel cell occurs when deformation energy applied to the membrane reaches a maximal value. The estimation of mechanical stress and deformation energy was made applying the modified Eyring equation [1]. The proposed model takes into account the influence of the temperature and water concentration on the membrane's mechanical properties. The water concentration in the membrane is simulated by considering water sorption/desorption kinetics and the water sorption isotherm of the membrane.

The model was applied to investigate the influence of thickness and operating conditions of periodic humidity cycling such as:

- Temperature
- Amplitude of the humidity variation in the cycle
- Cycle duration

on the lifetime of non-reinforced Nafion membrane.

The calculation results show that the mechanical durability of Nafion membrane increases as the membrane thickness increases and as the range of variation of humidity levels in the cycle decreases. The expected lifetime of a membrane increases as the temperature rises. The dependence of the expected membrane lifetime on the humidification cycle period passes through a minima, which is found between ca. 50–150 s, depending on the RH amplitude of the cycle and the average level of RH.

Acknowledgement

This work has been financially supported by Austrian Research Promotion Agency (FFG) and AVL List GmbH in the framework of IV2Splus Program, Grant No.835811 “A3 FALCON” (Advanced 3D Fuel Cell Analysis and Condition diagnostics).

The authors would like to thank Prof. Roldughin V.I. - Head of Laboratory of Physical Chemistry of Colloidal Systems at A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS (Russian Academy of Sciences) for the scientific discussion of the investigation and Sara Crockett for assistance with language editing and proofreading.

Thanks are also to the reviewers for helpful comments and suggestions to improve the manuscript.

REFERENCES

- [1] Burlatsky S, Gummalla M, O'Neill J, Atrazhev V, Varyukhin A, Dmitriev D, et al. A mathematical model for predicting the life of polymer electrolyte fuel cell membranes subjected to hydration cycling. *J Power Sources* 2012;215:135–44.
- [2] S T, Buechi FN, Inaba M. *Polymer electrolyte fuel cell durability*. New York. 2009.
- [3] Beuscher U, Cleghorn SJ, Johnson WB. Challenges for pem fuel cell membranes. *Int J Energ Res* 2005;29:1103–12.
- [4] Struis R, Quintilii M, Stucki S. Feasibility of li-nafion hollow fiber membranes in methanol synthesis: mechanical and thermal stability at elevated temperature and pressure. *J Membr Sci* 2000;177:215–23.
- [5] Barbi V, Funari SS, Gehrke R, Scharnagl N, Stribeck N. Nanostructure of nafion membrane material as a function of mechanical load studied by saxs. *Polymer* 2003;44:4853–61.
- [6] Haworth B, Gilbert M, Myers D. Melt-state shear flow and elasticity of a thermoplastic fluorosulphonated-ptfe copolymer. *J Mater Sci* 2005;40:955–64.
- [7] Huang X, Solasi R, Zou Y, Feshler M, Reifsnider K, Condit D, et al. Mechanical endurance of polymer electrolyte membrane and pem fuel cell durability. *J Polym Sci Part B: Polym Phys* 2006;44:2346–57.
- [8] Tang Y, Karlsson AM, Santare MH, Gilbert M, Cleghorn S, Johnson WB. An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane. *Mater. Sci. Eng., A* 2006;425:297–304.
- [9] Bograchev D, Gueguen M, Grandidier J-C, Martemianov S. Stress and plastic deformation of mea in fuel cells: stresses generated during cell assembly. *J Power Sources* 2008;180:393–401.
- [10] Marrony M, Barrera R, Quenet S, Ginocchio S, Montelatici L, Aslanides A. Durability study and lifetime prediction

- of baseline proton exchange membrane fuel cell under severe operating conditions. *J Power Sources* 2008;182:469–75.
- [11] Tang H, Pan M, Wang F, Shen PK, Jiang SP. Highly durable proton exchange membranes for low temperature fuel cells. *J Phys Chem B* 2007;111:8684–90.
- [12] Majsztrik PW, Bocarsly AB, Benziger JB. Viscoelastic response of nafion. effects of temperature and hydration on tensile creep. *Macromolecules* 2008;41:9849–62.
- [13] Satterfield MB, Benziger JB. Non-fickian water vapor sorption dynamics by nafion membranes. *J Phys Chem B* 2008;112:3693–704.
- [14] Kreuer K-D. The role of internal pressure for the hydration and transport properties of ionomers and polyelectrolytes, *Solid State Ionics*. In: *sSPC-16 Conference Proceedings [SSI] Special Issue*252(0); 2013. p. 93–101.
- [15] Safronova E, Golubenko D, Pourcelly G, Yaroslavtsev A. Mechanical properties and influence of straining on ion conductivity of perfluorosulfonic acid nafion[®]-type membranes depending on water uptake. *J Membr Sci* 2015;473:218–25.
- [16] Solasi R, Zou Y, Huang X, Reifsnider K. A time and hydration dependent viscoplastic model for polyelectrolyte membranes in fuel cells, *mech. Time-depend. Mater* 2008;12:15–30.
- [17] Khattra NS, Karlsson AM, Santare MH, Walsh P, Busby FC. Effect of time-dependent material properties on the mechanical behavior of pfsa membranes subjected to humidity cycling. *J Power Sources* 2012;214:365–76.
- [18] Sadiq Al-Baghdadi MA. A cfd study of hygro-thermal stresses distribution in pem fuel cell during regular cell operation. *Renew Energ* 2009;34:674–82.
- [19] Lai Y-H, Mittelsteadt CK, Gittleman CS, Dillard DA. Viscoelastic stress analysis of constrained proton exchange membranes under humidity cycling. *J Fuel Cell Sci Tech* 2009;6. 021002–21011–021002–13.
- [20] Kusoglu A, Tang Y, Santare MH, Karlsson AM, Cleghorn S, Johnson WB. Stress-strain behavior of perfluorosulfonic acid membranes at various temperatures and humidities: experiments and phenomenological modeling. *J Fuel Cell Sci Tech* 2009;6. 0110122–P11021–011012–8.
- [21] Kusoglu A, Tang Y, Lugo M, Karlsson AM, Santare MH, Cleghorn S, et al. Constitutive response and mechanical properties of pfsa membranes in liquid water. *J Power Sources* 2010;195:483–92.
- [22] Zhang X, Pisu P, Toops TJ. A study on a prognosis algorithm for pemfc lifetime prediction based on durability tests. *SAE Tech Pap* 2010. <http://dx.doi.org/10.4271/2010-01-0852>. 2010-01-0852.
- [23] Silberstein MN, Boyce MC. Constitutive modeling of the rate, temperature, and hydration dependent deformation response of nafion to monotonic and cyclic loading. *J Power Sources* 2010;195:5692–706.
- [24] Silberstein MN, Pillai PV, Boyce MC. Biaxial elastic–viscoplastic behavior of nafion membranes. *Polymer* 2011;52:529–39.
- [25] Silberstein MN, Boyce MC. Hygro-thermal mechanical behavior of nafion during constrained swelling. *J Power Sources* 2011;196:3452–60.
- [26] Lu Z, Lugo M, Santare MH, Karlsson AM, Busby FC, Walsh P. An experimental investigation of strain rate, temperature and humidity effects on the mechanical behavior of a perfluorosulfonic acid membrane. *J Power Sources* 2012;214:130–6.
- [27] Khattra NS, Lu Z, Karlsson AM, Santare MH, Busby FC, Schmiedel T. Time-dependent mechanical response of a composite {PFSa} membrane. *J Power Sources* 2013;228:256–69.
- [28] Klein M, Perrin J-C, Leclerc S, Guendouz L, Dillet J, Lottin O. Anisotropy of water self-diffusion in a nafion membrane under traction. *Macromolecules* 2013;46:9259–69.
- [29] Marrony M, Beretta D, Ginocchio S, Nedellec Y, Subianto S, Jones D. Lifetime prediction approach applied to the aquivion[™] short side chain perfluorosulfonic acid ionomer membrane for intermediate temperature proton exchange membrane fuel cell application. *Fuel Cells* 2013;13:1146–54.
- [30] Xiao P, Li J, Tang H, Wang Z, Pan M. Physically stable and high performance aquivion/epfme composite membrane for high temperature fuel cell application. *J Membr Sci* 2013;442:65–71.
- [31] Osborn SJ, Hassan MK, Divoux GM, Rhoades DW, Mauritz KA, Moore RB. Glass transition temperature of perfluorosulfonic acid ionomers. *Macromolecules* 2007;40 10:3886–90.
- [32] Matos B, Dresch M, Santiago E, Linardi M, de Florio D, Fonseca F. Nafion β -relaxation dependence on temperature and relative humidity studied by dielectric spectroscopy. *J Electrochem Soc* 2013;160 1:F43–8.
- [33] Matos B, Santiago E, Rey J, Fonseca F. Origin of α and β relaxations of nafion. *Phys Rev E* 2014;89 5:052601.
- [34] Page KA, Rowe BW, Masser KA, Faraone A. The effect of water content on chain dynamics in nafion membranes measured by neutron spin echo and dielectric spectroscopy. *J Pol Science Part B: Polym Phys* 2014;52 9:624–32.
- [35] Roylance D. Engineering viscoelasticity, department of materials science and engineering–Massachusetts institute of technology. *Camb MA* 2001;2139:1–37.
- [36] Sethuraman VA, Weidner JW, Haug AT, Protsailo LV. Durability of perfluorosulfonic acid and hydrocarbon membranes: effect of humidity and temperature. *J Electrochem Soc* 2008;155:B119–24.
- [37] Karpenko-Jereb L, Innerwinkler P, Kelterer A-M, Sternig C, Fink C, Prenninger P, et al. A novel membrane transport model for polymer electrolyte fuel cell simulations. *Int J Hydrogen Energy* 2014;39 13:7077–88.
- [38] Panha K, Fowler M, Yuan X-Z, Wang H. Accelerated durability testing via reactants relative humidity cycling on pem fuel cells. *Appl Energy* 2012;93:90–7.
- [39] Macauley N, Alavijeh AS, Watson M, Kolodziej J, Lauritzen M, Knights S, et al. Accelerated membrane durability testing of heavy duty fuel cells. *J Electrochem Soc* 2015;162 1:F98–107.
- [40] Aindow T, O'Neill J. Use of mechanical tests to predict durability of polymer fuel cell membranes under humidity cycling. *J Power Sources* 2011;196 8:3851–4.
- [41] Ralph T, Barnwell D, Bouwman P, Hodgkinson A, Petch M, Pollington M. Reinforced membrane durability in proton exchange membrane fuel cell stacks for automotive applications. *J Electrochem Soc* 2008;155 4:B411–22.